THORIUM AND URANIUM SEPARATION FROM RARE EARTH COMPLEX MıNERALS IN TURKEY

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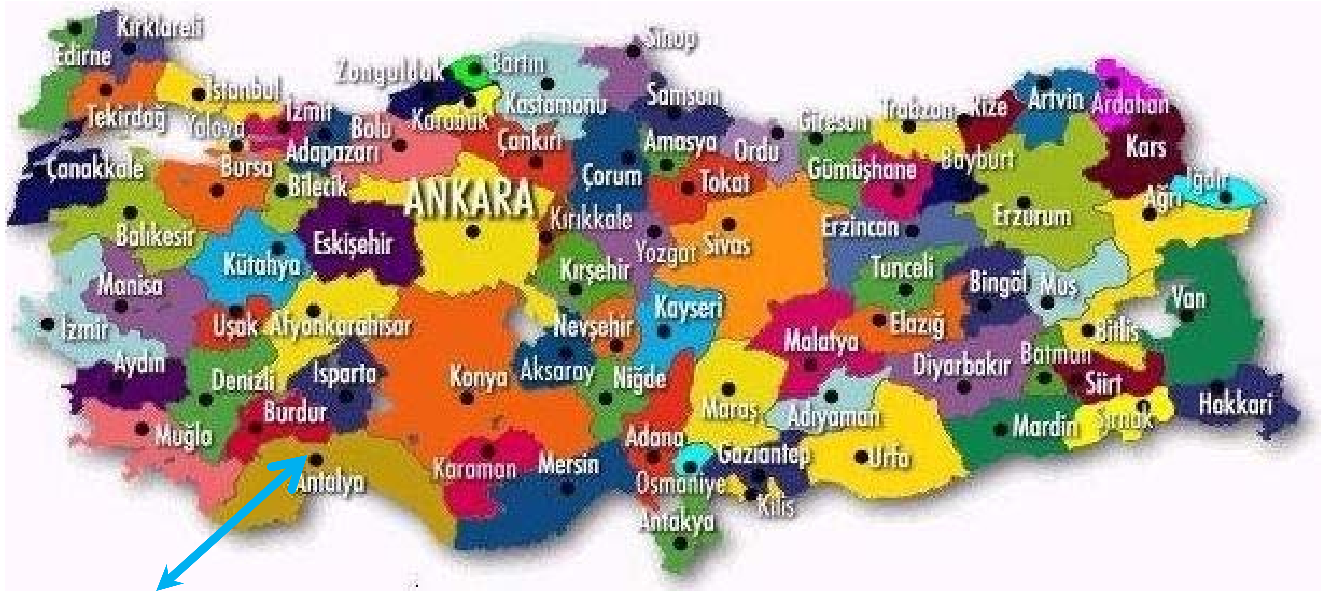
International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues

IAEA CN-216, Vienna

23-27 June 2014

AMR
AKSU-DIAMAS REE+TH DEPOSIT

- AMR ore mineral deposit in the southern part of Turkey, contains allanite-chevkinite and titanite as rare earth containing minerals. Estimated reserv for REEs: 345.000 t (Çanakli-I and –II areas)
- for Th: 20.000 t and U: 5400 t.



MINERALOGY OF THE GRAVITY CONCENTRATE

Component	Element, Wt. %	Oxide, Wt. %	Mineral	Minerals, Wt. %
Rare Earths	1.86	2.17	Allanite-Chevkinite	4-5
Zircon	8.17	11	Zircon	20
Titanium		8.02	Titanite	20
Thorium	0.19	0.22	Thorite	0.3
Niobium	0.1	0.14	Betafite	0.3
Uranium	0.05	0.06	Betafite-Uranothorite	0.3
Hafnium	0.1	0.12	Zircon	20
Iron Oxide	18.77	18.77		

PHYSICAL BENEFICIATION

FLOTATION CONCENTRATE

Element	% or ppm	Element	% or ppm
Fe_2O_3 [%]	14,5	Sm	583
TiO_2 [%]	13,4	Eu	110
Zr	4854	Gd	352
Th	1496	Tb	39
U	416,1	Dy	173
Y	787	Ho	32
La	7735	Er	87
Ce	12698	Yb	92
Pr	1407	Tm	14
Nd	4542	ΣREEs	~2.9%

HYDROMETALLURGICAL PROCESS

CAUSTIC CRACKING

- In order to obtain a chemical concentrate of REEs, chemical processes should be applied to the AMR concentrate.
- Silicate is predominant constituent of almost all valuable elements in the concentrate.
- Caustic cracking has been applied to the concentrate:

$(M1,M2)(SiO_3)_n + mNaOH \rightarrow (M1,M2)(OH)_n + (nxm)Na_2SiO_3$

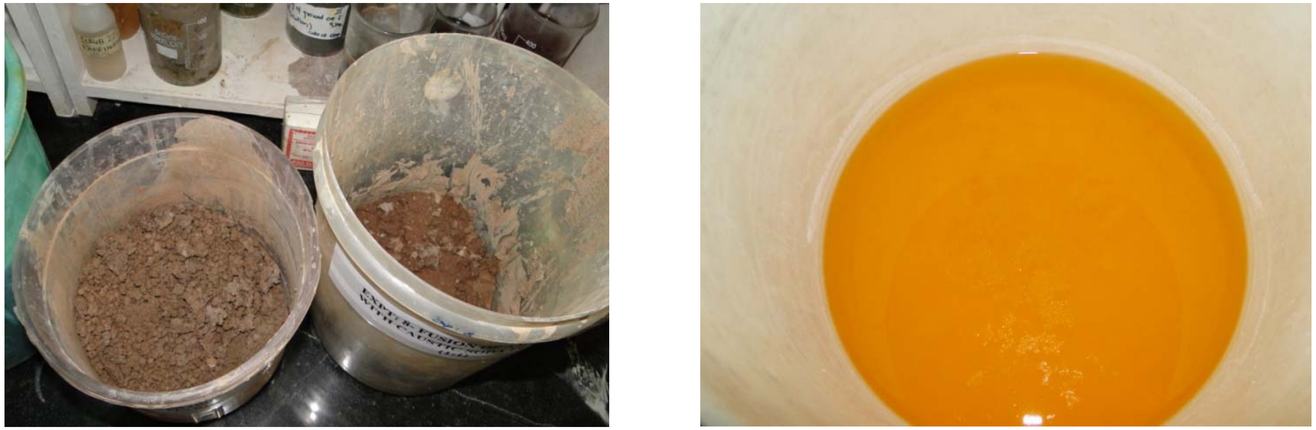
  - Water leaching for separating the greatest part of silicate as water soluble sodium silicate and transform the valuable elements (Zr, Ti, REEs, Th, U as well as Fe, etc.) to their hydroxides.

HYDROMETALLURGICAL PROCESS

ACID LEACHING

- The cake which contains metal hydroxides and untransformed gangue minerals is filtered off and dried.
- The dried cake is then treated with hydrochloric acid to dissolve the metal hydroxides for further separation operations

$$(M1,M2)(OH)_n + nHCl \longrightarrow (M1,M2)Cl_n + (n/2)H_2O$$



HYDROMETALLURGICAL PROCESS

TREATMENT OF CHLORIDE SOLUTION

- Before oxalate precipitation REEs+Th chloride solution is treated for removal of excess iron, zirconium, uranium and titanium.
- Iron (III) chloride is removed firstly by TBP solvent extraction

Typical composition of

Iron free solution

Element	mg/L
Ti	3126
Zr	1561
U	85
Th	133,5
Y	64,6
La	710,7
Ce	1257,2
Pr	87,8
Nd	287,7

HYDROMETALLURGICAL PROCESS ZR, TI AND U SEPARATION

- Hot phtalic acid solution is added to chloride solution and most of Ti, Zr and U are precipitated and filtered off.
- Metal phtalates are treated with NaOH solution to convert into their relative hydroxides.
- While Ti, Zr and Uranyl hydroxides are being removed from the solution, the phtalate solution is treated with HCl to reclaim phtalic acid.

HYDROMETALLURGICAL PROCESS SEPARATION OF U

- Hydroxide cake of Zr, Ti and U is dissolved in diluted nitric acid.
- Nitrate solution is fed for SX unit using TBP as extractant.
- During this operation Zr and U are completely extracted into the organic phase, while Ti remaining in the aqueous phase.
- First Zr is selectively stripped from organic phase, followed by U stripping by using different stripping solution for an accurate separation.
- Finally, U is precipitated as ammonium diurante (ADU).

HYDROMETALLURGICAL PROCESS

OXALATE PRECIPITATION

- A strong solution of oxalic acid is added to the chloride solution of REEs+Th obtained after Fe, Zr and Ti removal.
  - continuous stirring at 80 °C
  - Filtration of oxalate precipitate at 40-60 °C
  - Washing with hot water
  - Analysis of a precipitate sample at ICP-MS

Typical composition of [REEs+Th]oxalate

Element	Mass [mg]	Relative concentration of elements [%]	Element	Mass [mg]	Relative concentration of elements [%]
Y	4,13	0,98	Dy	0,97	0,23
La	29,46	7,00	Ho	0,16	0,04
Ce	69,29	16,47	Er	0,52	0,12
Pr	7,03	1,67	Tm	0,08	0,02
Nd	27,74	6,59	Yb	0,53	0,13
Sm	3,18	0,76	Lu	0,06	0,01
Eu	0,6	0,14	Th	8,6	2,04
Gd	2,02	0,48	Sc	2,73	0,65
Tb	0,22	0,05	ΣREE+Th	157,32	37,40
			REE+Th Oxalate	**420,64**	**100,00**

METATHESIS OF OXALATES

- Rationale of metathesis:
  - Transform the oxalate compounds to easy soluble hydroxide compounds
  - Preparing REEs chloride solution for subsequent SX by using EHEHPA
  - Reclaiming alkali oxalate for reducing cost of chemicals
- REEs+Th oxalate precipitate is heated with 60% NaOH (w/v) with continuous stirring
  - For 4 hrs at 100 °C
  - Aging 4 hrs at 50-60 °C
- Filtering and washing with hot water
- Wet hydroxide cake is dissolved in diluted HCl (5-6 N) at 35-40 °C (reaction heat)

THORIUM SEPARATION

- Th(IV) hydroxide solubility is decreasing sharply by increasing pH even in acidic region
- pH regulation is used to precipitate almost completely Th as its hydroxide from $RECl_3$ and $ThCl_4$ solution
  - 5 M NaOH (or NH_4OH) solution is added to mixed chloride solution
  - the precipitation ends at pH≈4,2-4,5
- The precipitation yield of thorium is found as high as 99%.
- But appreciable amount of Ce and other light REEs come along with thorium and they represent 40-45 % of crude Th hydroxide precipitate.

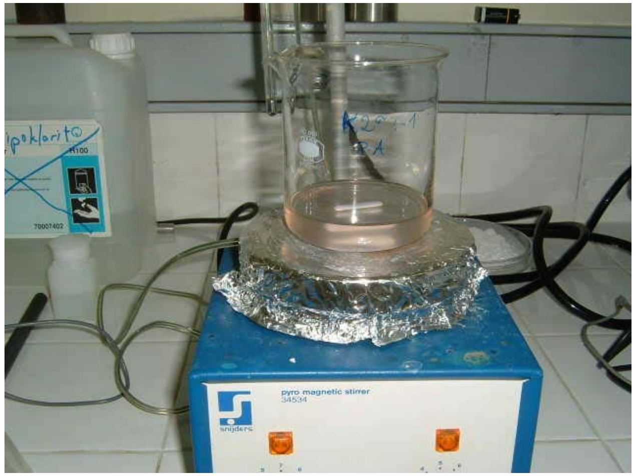
THORIUM PURIFICATION

- Rationale of Th purification:
  - Reclaiming mixed rare earths
- Crude Th hydroxide cake is dissolved in conc. HNO_3 and thorium peroxide precipitation is applied
- The optimum Th peroxide formation is found at pH between 0,9-1,2 which is adjusted by ammoniac solution at 60 °C and realized with 35% H_2O_2 solution.
- Thorium precipitation yield is about 98%.
- Thorium precipitate should be thoroughly washed with 2% NH_4NO_3 solution and the filtrate containing REEs can be recycled to feed (REEs+Th) chloride solution.

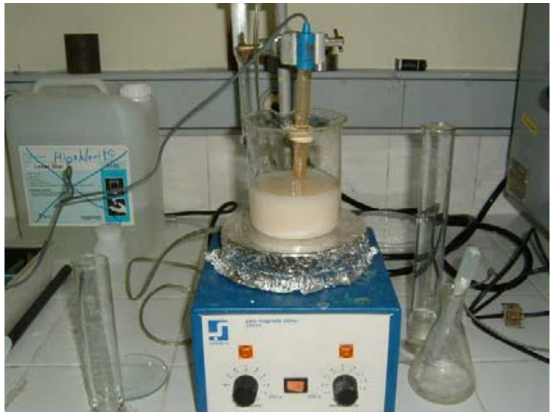
COMPOSITION OF THORIUM PRODUCT

Oxide	%
ThO_2	96
Ce_2O_3	2,2
La_2O_3	1,4
Pr_6O_{11}	0,07
Nd_2O_3	0,4

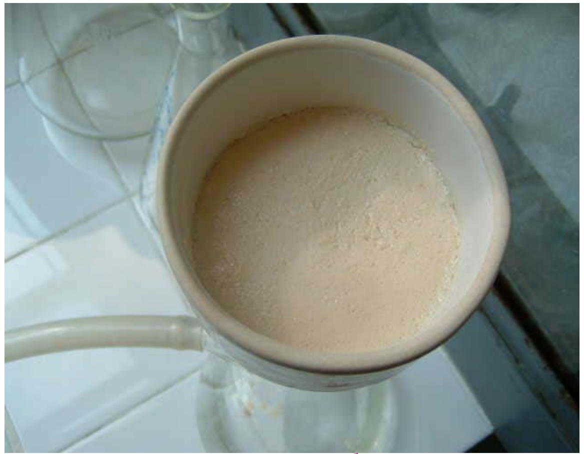
THORIUM PURIFICATION



Th nitrate solution pH regulation



Th peroxide precipitation by H_2O_2 addition



Filtration of Th peroxide precipitate

CONCLUSION

- Thorium and uranium separation from a REEs solution is possible in by using simple traditional methods
- Main advantage of this method is to separate with high recovery yield uranium and almost completely thorium which is an undesirable element due to its radioactive property in the different REEs group or individual REE.
- Separation of thorium **before** any other step of REE's group or individual element separation is crucial
- By using this flowsheet it would be possible to obtain uranium and other valuable elements (Zr, Ti, etc.) as co-products of REEs.
- Another important point, during REEs production, it is avoided to accumalate U and Th contaminated process wastes.
- Thus, in the contrary, radioactive elements are refined and contained for safe storage.

THANK YOU FOR YOUR ATTENTION

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